Performance of Sorption Layer Using Ca/Mg Immobilizing Agent against Natural Contamination

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Abstract

Soils and rocks containing heavy metals and metalloids derived from nature were often generated in huge volumes from excavation works. Without proper treatment, these soils may generate hazardous leachate and cause environmental contamination. Sorption layer method, which has been developed recently, utilizes a permeable soil layer with sorption capacity lying beneath piled soil and rock in embankments to retain the chemicals of concern dissolved in the leachate. Immobilizing agent and mineral are used solely or by mixing with a clean host soil to strengthen the sorption capacity. Permeability and equilibrium sorption characteristics of the sorption layer material are fundamental factors affecting its sorption. Thus, this paper addresses experimental results on permeability and equilibrium sorption characteristics of the decomposed granite soil enhanced by the Ca/Mg composite immobilizing agent. Experimental results showed that higher immobilizing agent content exhibited the higher sorption capacity, both curing period and mixing ratio has no obvious effect on hydraulic conductivity of the mixture.

Keywords: natural contamination, immobilizing agent, hydraulic conductivity, sorption layer

1. Introduction

Soils and rocks containing heavy metals (e.g. lead, cadmium) and/or metalloids (e.g. arsenic, selenium) derived from nature due to their geologic histories are widely distributed in Japan. Once they are excavated in construction works such as tunnel construction, leaching of these metals may be triggered due to oxidization and decomposition of sulfide minerals contained in some soils and rocks. Without proper managements and/or treatments for them, they will generate acid leachate containing unacceptable concentrations of heavy metals and/or metalloids, which are higher than the environmental standards.
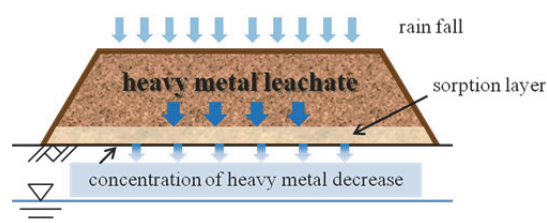
Remediation of soils containing natural derived heavy metals has become a subject under the control of the Amending Soil Contamination Countermeasures Act issued by the Japan Ministry of the Environment in 2010, which proposes several countermeasures for these soils including containment method, insolubilization method, and etc. Containment method uses seepage control works to reduce generation of leachate, and low-permeable soil layers or geomembrane sheets to prevent migration of

the leachate into the surrounding environment. However, the potential slope failure due to low interface friction between piled soils/rocks and geomembrane sheets is a major concern. In addition, its execution cost is hard to afford when treating a huge amount of excavated soils. Insolubilization methods apply solidification and/or stabilization agents to fix the heavy metal contained in contaminated soils and reduce the leaching potential. Its long-term performance under field conditions is not fully verified and has been a main concern.
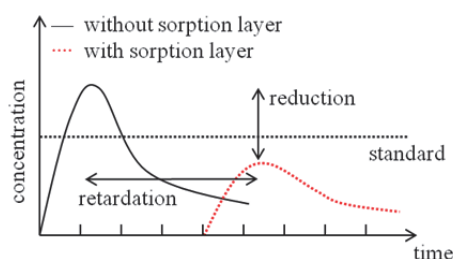
Sorption layer method is a newly developed technology for in situ containment of excavated soils and rocks (Technical Committee of Environmental Conservation Technology Association, Hokkaido 2012). It utilizes a permeable soil layer with sorption capacity for contaminants of concern underlying the piled soils and rocks in embankment (Fig. 1(a)). The composition of this layer can be natural material (soil, minerals), artificial material (immobilizing agents) or the mixture of them. Rainfall infiltration is limited by soil cover to avoid generating more leachate.

The sorption layer should have a sorption capacity high enough to retain the leachable amount of

contaminants to the acceptable level. The process is similar to that of a horizontally placed permeable reactive barrier, where the leachate can pass the sorption layer under a certain velocity and contaminants of concern is decomposed or sorbed by the composition material of the layer during permeation. The concentration of contaminant in the leachate should be lowered, and the time when the contaminants reach the surrounding environment should also be retarded. The effluent flowing out of the sorption layer is expected to meet the environmental standard (Fig. 1(b)).

(a) Schematic diagram of the sorption layer method

(b) Effect of the sorption layer (Revised from Igarashi and Mikami (2004))

Fig.1 Conception of sorption layer method

The definitive aim of this method is not to completely block the contaminants, but to lower their concentrations to an acceptable level. When certain working conditions for the sorption layer method can be met, its advantage of easy construction, low cost and good stability make this method act as an economical countermeasure for huge amount of excavated soils and rocks, although some technical issues should be addressed.

An Immobilizing or stabilizing agent is often employed to strengthen the sorption capacity as well as the bearing capacity of the sorption layer by mixing with a clean host soil. In conventional immobilization or stabilization practices, performance of immobilizing agents has been evaluated after mixing it directly with contaminated soils. However the process of the sorption layer is quite different because the contaminants dissolved in the leachate contact the soil-agent mixture. Thus, how this different process affects the sorption performance is needed to be studied. Particularly, the hydraulic performances should be preliminarily evaluated to ensure whether the leachate flows through the sorption layer

continuously as expected, since and flow conditions (flow rate, retention time, etc.) are known as key issues for the sorption performance.

This study was conducted to evaluate the performance of the sorption layer, which was prepared by mixing a typical soil, decomposed granite soil, with the Ca/Mg composite immobilizing agent (The Society of Material Science, Japan 2014). The authors verified that this Ca/Mg composite immobilizing agent was able to immobilize both metal cations and anions in water-soluble forms (Bobea et al. 2012). Thus, the agent is expected to effectively immobilize lead, arsenic, and fluoride, which are typically contained in the leachate of soils and rocks. The specific objective of this paper is to obtain both hydraulic and equilibrium sorption performances of the soil-immobilizing agent mixture, influenced by mixing ratio of the agent and curing period after mixing. As a trace metal, arsenic was selected, since it is most frequently contained in naturally contaminated soils and rocks found in Japan.

2. Materials and Methods

2.1 Materials

Ca/Mg composite immobilizing agent, which was manufactured through calcination of selected natural minerals by Sumitomo Osaka Cement Co., Ltd., Japan, was used. Properties of the material are shown in Table 1 (The Society of Materials Science, Japan, 2014).

Table 1 Properties of Ca/Mg composite immobilizing agent

Items	Standard/Method	Value
Bulk density	JIS R 9301(untamped)	0.90 g/cm^3
pH (25 $^\circ$C)	1 g in 100 mL water Mixing 1 hour	10.3
Blaine's specific surface area	JIS R 5201	4200 cm^2/g
Water content	5g, Dried under 110°C	0.21 wt%
Main component	JIS R 9011	
CaO		35.6 %
MgO		19.4 %
SO$_3$		3.98 %
Fe$_2$O$_3$		3.73 %
SiO$_2$		1.52 %
Al$_2$O$_3$		0.068 %
P$_2$O$_5$		0.035 %
Ignition loss		33.5 %

Commercially available decomposed granite soil (particle density, ρ_s = 2.70 Mg/m^3) was used as a host soil. Soil particles which passed a 2 mm-opening sieve were used. The particle size distribution curve of decomposed granite soil after sieving is shown in Fig. 2. The pH of the suspended soils in the liquid to solid ratio (L/S) = 5 according to JGS 0211 (2009)
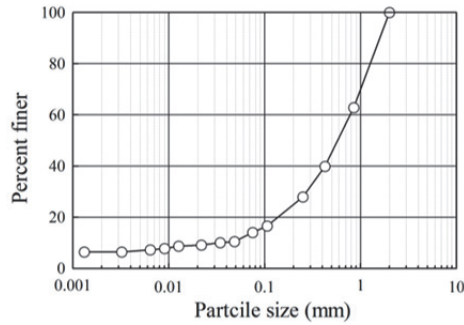
was 9.5.

Fig. 2 Particle size distribution of the decomposed granite soil after sieving

2.2 Methods

(1) Hydraulic conductivity test

Hydraulic conductivity tests were conducted according to ASTM D 5084 "Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter" (Fig. 3). The hydraulic gradient is set to 5 and the cell pressure of 30 kPa was applied. Distilled water was used as permeant solution.
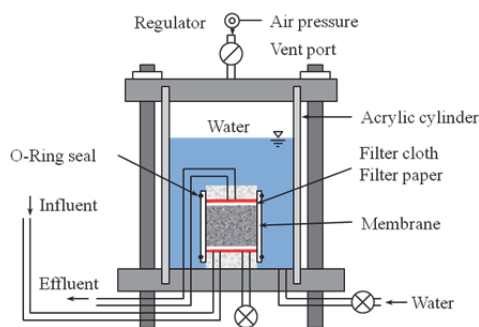

Fig. 3 Schematic view of a flexible-wall permeameter

The immobilizing agent was mixed with the air-dried soil by 0%, 3% and 5% of its dry weight. Water content of the mixture was adjusted to its optimum water content (10.1 to 11.3%), which was determined by the A-a method of JIS A 1210 (2009), by adding distilled water. Then, the mixture was compacted in a cylindrical mold in three layers. The dimension of the mold is 6 cm in diameter and 7 cm in height. The compaction degree was set to 95%. After compaction, cling film was used to wrap the mold, and the specimen was kept in a fully-sealed plastic box to be cured for 0 or 7 days.

After curing, the specimen was submerged in distilled water and saturated by vacuum deaeration for at least 24 hours. Then, the specimen was set on the flexible-wall permeameter. It was sandwiched with filter papers, filter clothes, porous caps and pedestals, confined by a latex membrane on the sides. Permeation was conducted until hydraulic conductivity value was stable and 5 or more pore volumes of flow were permeated.

(2) Batch sorption test

The preparation of specimens was similar to that for the hydraulic conductivity test, except that the specimen dimension was 5 cm in diameter and 10 cm in height, and the specimens were cured after taking them out of the mold. After curing, specimens were crushed ($\leq$ 2mm) and mixed with the $NaAsO_2$ solution in $L/S = 20$. The concentration of the solution is 0.1, 0.5, 1, 5 and 10 mg/L. The samples were subjected to 24 hours horizontal shaking at 150 rpm, then left for 15 minutes. Solid-liquid separation was done by centrifugation under 3,000 rpm for 20 minutes and filtering using a 0.45μm-opening membrane filter. Arsenic concentrations before and after the sorption test were analyzed by an atomic absorption spectrometry (AAS) method (SHIMAZU, AA-6800).

3. Results and Discussion

3.1 Hydraulic conductivity

For each mixing ratio (0, 3, and 5%) and curing period (0 and 7 days), the tests were conducted in duplicate.

The variation of average hydraulic conductivity values with different mixing ratios and curing periods was presented in Fig. 4.
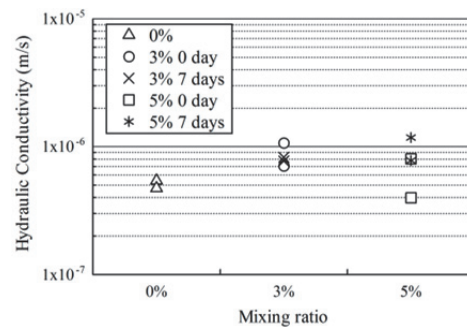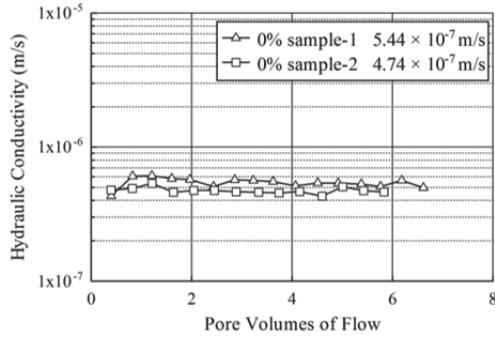

Fig. 4 Hydraulic conductivity variation among different cases

The hydraulic conductivity of 0-day and 7-day curing specimens were almost same, which indicates that 7-day curing has no obvious effect, although the unconfined compression strength increased by 7-day curing (Mo et al. 2014). Considering that the hydraulic conductivity tests lasted for several days, hydration reactions could happen during permeation even in 0-day curing specimens. Thus, the microstructure of the specimens with or without curing, and accordingly hydraulic conductivity values became similar.
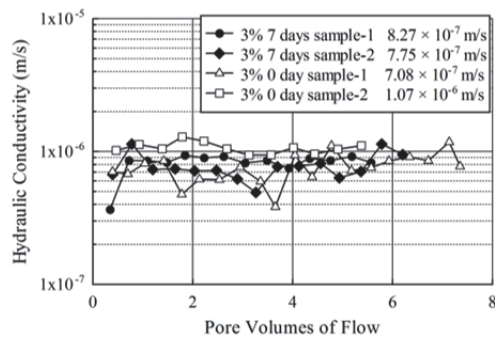
The hydraulic conductivity of 0% case was relatively lower than 3% and 5% cases for most samples. This is probably due to aggregation after addition of the immobilizing agent. However, the similar results between 3% and 5% cases indicate that mixing ratio has no obvious effect on the hydraulic

conductivity and the extent of hydration reactions was similar. This is probably because the total amount of silicate offered by the decomposed granite soil was almost same in both 3% and 5% cases, and the hydration reactions were limited to the same extent.
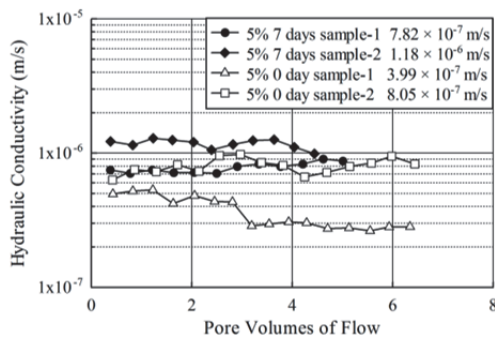
The variation of hydraulic conductivity with pore volumes of flow and the average hydraulic conductivity value obtained for each case were shown in Fig. 5.

(a) Hydraulic conductivity of samples with mixing ratio of 0% (decomposed granite soil after compaction)

(b) Hydraulic conductivity of samples with mixing ratio of 3%

(c) Hydraulic conductivity of samples with mixing ratio of 5%

Fig. 5 Hydraulic conductivity of samples with mixing ratio of 0%, 3% and 5%

Variation of the hydraulic conductivity of different

cases is within one order between 1×10^{-6} m/s to 1×10^{-7} m/s and almost constant throughout the test period, which indicates that the addition of the Ca/Ma immobilizing agent does not significantly decrease the hydraulic conductivity. This trend is preferable for the sorption layer application, since the leachate should flow through the sorption layer preferentially for the metals of concern to be sorbed. If the hydraulic conductivity is decreased with time by adding the agent, the leachate is unlikely to flow through the sorption layer and the sorption capacity cannot be fully mobilized.

3.2 Sorption performance

Sorption isotherms were determined by an empirical relation between the equilibrium concentration of the solute and the sorbed amount, based on Freundlich equation, which is expressed as follows:

$$S = kC_{eq}^{\ n} \tag{1}$$

where S is the sorbed amount (mg/g), C_{eq} is the equilibrium concentration of the solute (mg/L), k and n are constants.

Sorption isotherms in linear scales for all samples with the mixing ratio of 0%, 3% and 5%, which were cured for 0 or 7 days, with the equilibrium concentrations ranging from 0 to 1 mg/L are summarized in Fig. 6.
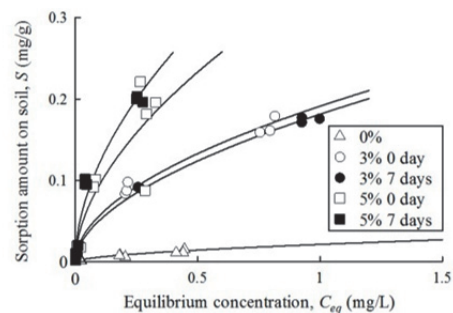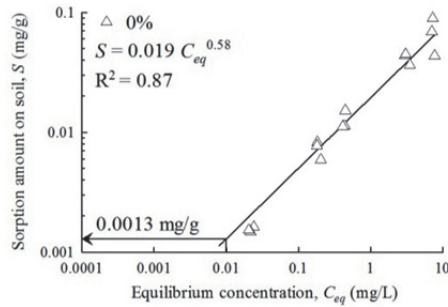

Fig. 6 Comparison of sorption isotherms of different cases

Sorption isotherms of different cases in log scales are shown in Fig. 7, which includes the sorbed amount (S) for the equilibrium concentration (C_{eq}) of 0.01 mg/L, which equals to the environmental standard of arsenic for soil and groundwater quality, Japan.
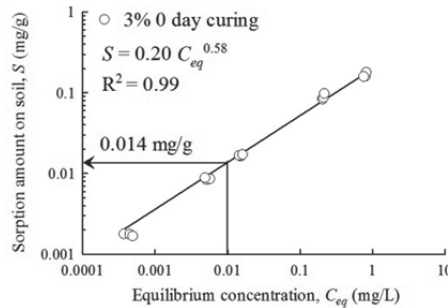
There are three possible mechanisms responsible for the sorption of arsenic by the Ca/Mg immobilizing agent. First is the precipitation between calcium and arsenic. Second is the surface attraction of arsenic with magnesium hydroxide. Third is the surface attraction of arsenic on the hydration products.

It can be observed from Fig. 6 and 7 that adding the agent clearly strengthens the sorption ability of the mixture. This is because the higher immobilizing
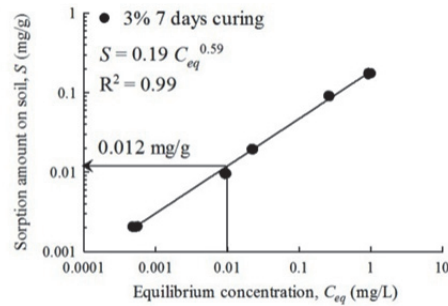
agent content provides more available calcium and magnesium that promote the sorption of arsenic. However, the effect of curing time is not obvious, which implies that the sorption effect of hydration products is not obvious.
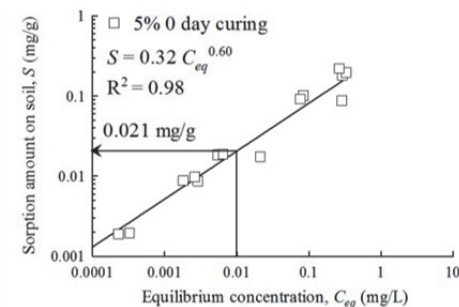

(a) Sorption isotherm for sample with mixing ratio of 0%
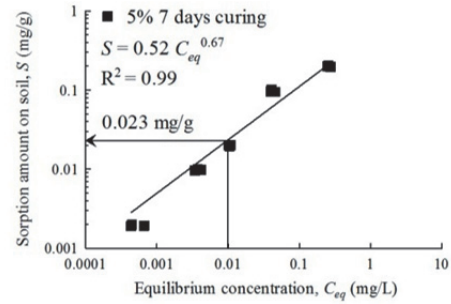

(b) Sorption isotherm for sample with mixing ratio of 3% and 0-day curing

(c) Sorption isotherm for sample with mixing ratio of 3% and 7-day curing

(d) Sorption isotherm for sample with mixing ratio of 5% and 0-day curing

(e) Sorption isotherm for sample with mixing ratio of 5% and 7-day curing

Fig. 7 Sorption isotherms for samples with different mixing ratio and curing periods

The less effect of curing time could be explained by two possible reasons. The first one is related to the experimental procedure of batch sorption test. Hydration reactions and crystallization that occurred during curing and the generated calcium/magnesium silicate hydrates were damaged by crushing and shaking, and the effect of high specific surface area of the hydrates and the positive charge of the surface to catch arsenic may be offset. The second reason is that there is not enough Ca^{2+} to either overcompensation of the hydrate surface or participate in the chemical reaction. Surface of calcium/magnesium silicate hydrate remains negatively charged, which are unable to attract arsenic oxyanion onto its surface.

Thus, sorption onto the surface of hydration products is not the main mechanism of arsenic sorption. The precipitation of arsenic with calcium and sorption onto the surface of magnesium hydroxide should have the major effect.

Electrical conductivity (EC) variations of the solution before and after sorption under different initial $NaAsO_2$ concentration are shown in Fig. 8.
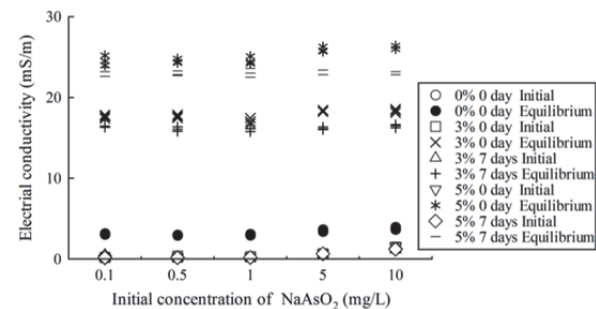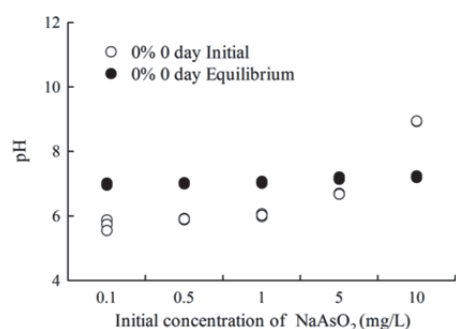
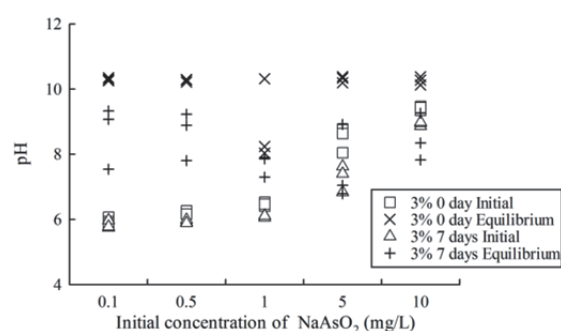

Fig. 8 Variation of EC before and after sorption

EC value is relatively low for initial solution. After sorption, EC values of 3% and 5% case increased greatly compared to 0% case, which indicates that adding the agent provides more available calcium and magnesium and promotes the sorption of arsenic. The higher equilibrium EC value

of 5% case indicates that more available calcium remaining in the solution, which corresponds to its stronger sorption performance. Thus, the sorption performance of the mixture was strengthened with addition of the agent and more calcium offered.
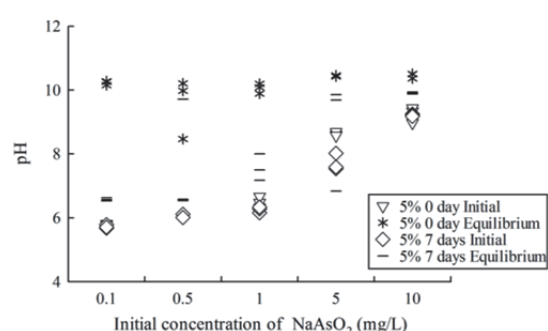
EC values of 0 day curing case are higher than 7 days curing case, which is probably caused by the hydration process that consumed more calcium and magnesium. Thus, their concentrations in the final solution decreased, which can also be reflected by the pH variation shown in Fig. 9.

(a) Variation of pH before and after sorption of samples with mixing ratio of 0%

(b) Variation of pH before and after sorption of samples with mixing ratio of 3%

(c) Variation of pH before and after sorption of samples with mixing ratio of 5%

Fig. 9 Variation of pH before and after sorption

The pH of final solution of 0 day curing cases is higher than 7 days curing cases, which is caused by higher concentration of calcium and magnesium.

4. Conclusions

This research was conducted to evaluate the effectiveness of the soil improved by the Ca/Mg composite immobilizing agent as a sorption layer against natural contamination. Particularly, the permeability and equilibrium sorption characteristics of the sorption layer were studied.

Hydraulic conductivity of the soil-immobilizing agent mixture was around 1×10^{-6} to 1×10^{-7} m/s. Adding the agent with 5% in dry weight basis in maximum has no obvious effect on the hydraulic conductivity. Higher immobilizing agent content corresponds to higher sorption capacity. However, curing periods has a minor effect in batch test. Formation of precipitation between arsenic with calcium and surface attraction on magnesium hydroxide is the major mechanism of sorption.

Future researches should evaluate the performance of sorption layer affected by leachate pH, co-existing ions, and dynamic sorption characteristics. An accurate and reliable design method considering complicated and filed conditions such as unsaturated flow needs to be proposed in order to promote the application of sorption layer.

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